7.7: Formation Reactions

Learning Objectives

- Define a *formation reaction* and be able to recognize one.
- Use enthalpies of formation to determine the enthalpy of reaction.

Hess's law allows us to construct new chemical reactions and predict what their enthalpies of reaction will be. This is a very useful tool because it is not necessary to measure the enthalpy changes of every possible reaction. We need measure only the enthalpy changes of certain benchmark reactions, and then use these reactions to algebraically construct any possible reaction and combine the enthalpies of the benchmark reactions accordingly.

But what are the benchmark reactions? We need to have some agreed-on sets of reactions that provide the central data for any thermochemical equation.

Formation reactions are chemical reactions that form one mole of a substance from its constituent elements in their standard states. The term *standard states* means as a diatomic molecule, if that is how the element exists, and in the proper phase at normal temperatures (typically room temperature). The product is one mole of substance, which may require that coefficients on the reactant side be fractional (a change from our normal insistence that all coefficients be whole numbers). For example, the formation reaction for methane ($\mathrm{CH_4}$) is

$$\mathrm{C(s) + 2\,H_2(g) \rightarrow CH_4(g)}$$

The formation reaction for carbon dioxide ($\mathrm{CO_2}$) is

$$\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$$

In both cases, one of the elements is a diatomic molecule because that is the standard state for that particular element. The formation reaction for $\mathrm{H_2O}$:

$$\mathrm{2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)}$$

—is *not* in a standard state because the coefficient on the product is 2; for a proper formation reaction, only one mole of product is formed. Thus, we have to divide all coefficients by 2:

$$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(\ell)}$$

On a molecular scale, we are using half of an oxygen molecule, which may be problematic to visualize. However, on a molar level, it implies that we are reacting only half of a mole of oxygen molecules, which should be an easy concept for us to understand.

Example 7.7.1

Which of the following are proper formation reactions?

a. $\mathrm{H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)}$
b. $\mathrm{Si(s) + 2\,F_2(g) \rightarrow SiF_4(g)}$
c. $\mathrm{CaO(s) + CO_2 \rightarrow CaCO_3(s)}$

Solution

a. In this reaction, two moles of product are produced, so this is not a proper formation reaction.
b. In this reaction, one mole of a substance is produced from its elements in their standard states, so this is a proper formation reaction.
c. One mole of a substance is produced, but it is produced from two other compounds, not its elements. So this is not a proper formation reaction.

Exercise 7.7.1

Is this a proper formation reaction? Explain why or why not.

$$\mathrm{2\,Fe(s) + 3\,P(s) + 12\,O(g) \rightarrow Fe_2(PO_4)_3(s)}$$

Answer

This is not a proper formation reaction because oxygen is not written as a diatomic molecule.

Given the formula of any substance, you should be able to write the proper formation reaction for that substance.

Example 7.7.2

Write formation reactions for each of the following.

a. $\mathrm{FeO(s)}$
b. $\mathrm{C_2H_6(g)}$

Solution

In both cases, there is one mole of the substance as product, and the coefficients of the reactants may have to be fractional to balance the reaction.

a. $\mathrm{Fe(s) + \tfrac{1}{2}O_2(g) \rightarrow FeO(s)}$
b. $\mathrm{2\,C(s) + 3\,H_2(g) \rightarrow C_2H_6(g)}$

Exercise 7.7.2

Write the equation for the formation of $\mathrm{CaCO_3(s)}$.

Answer

$$\mathrm{Ca(s) + C(s) + \tfrac{3}{2}O_2(g) \rightarrow CaCO_3(s)}$$

The enthalpy change for a formation reaction is called the **enthalpy of formation** and is given the symbol ΔH_f. The subscript *f* is the clue that the reaction of interest is a formation reaction. Thus, for the formation of FeO(s),

$$Fe(s) + \frac{1}{2}O_2(g) \rightarrow FeO(s) \quad \Delta H = \Delta H_f = -272 kJ/mol$$

Note that now we are using kJ/mol as the unit because it is understood that the enthalpy change is for one mole of substance. Note, too, by definition, that the enthalpy of formation of an element is exactly zero because making an element from an element is no change. For example,

$$H_2(g) \rightarrow H_2(g) \; \Delta H_f = 0$$

Formation reactions and their enthalpies are important because *these are the thermochemical data that are tabulated* for any chemical reaction. Table 7.7.1 - Enthalpies of Formation for Various Substances, lists some enthalpies of formation for a variety of substances; in some cases, however, phases can be important (e.g., for H_2O).

It is easy to show that any general chemical equation can be written in terms of the formation reactions of its reactants and products, some of them reversed (which means the sign must change in accordance with Hess's law). For example, consider

$$2NO_2(g) \rightarrow N_2O_4(g)$$

We can write it in terms of the (reverse) formation reaction of NO_2 and the formation reaction of N_2O_4:

$$\begin{array}{ll} 2\times\left[NO_2(g)\rightarrow \frac{1}{2}N_2(g)+O_2(g)\right] & \Delta H=-2\times\Delta H_r\left[NO_2\right]=-2(33.1kJ) \\ N_2(g)+2O_2(g)\rightarrow N_2O_4(g) & \Delta H=\Delta H_r\left[N_2O_4\right] \quad =9.1kJ \\ \hline 2NO_2(g)\rightarrow N_2O_4 & \Delta H=-57.1kJ \end{array}$$

We must multiply the first reaction by 2 to get the correct overall balanced equation. We are simply using Hess's law in combining the ΔH_f values of the formation reactions.

Table 7.7.1 Enthalpies of Formation for Various Substances

Compound	ΔH_f (kJ/mol)	Compound	ΔH_f (kJ/mol)	Compound	ΔH_f (kJ/mol)	Compound	ΔH_f (kJ/mol)
Ag(s)	0	Ca(s)	0	Hg_2Cl_2(s)	−265.37	$NaHCO_3$(s)	−950.81
AgBr(s)	−100.37	$CaCl_2$(s)	−795.80	I_2(s)	0	NaN_3(s)	21.71
AgCl(s)	−127.01	$CaCO_3$(s, arag)	−1,207.1	K(s)	0	Na_2CO_3(s)	−1,130.77
Al(s)	0	$CaCO_3$(s, calc)	−1,206.9	KBr(s)	−393.8	Na_2O(s)	−417.98
Al_2O_3(s)	−1,675.7	Cl_2(g)	0	KCl(s)	−436.5	Na_2SO_4(s)	−331.64
Ar(g)	0	Cr(s)	0	KF(s)	−567.3	Ne(g)	0
Au(s)	0	Cr_2O_3(s)	−1,134.70	KI(s)	−327.9	Ni(s)	0
$BaSO_4$(s)	−1,473.19	Cs(s)	0	Li(s)	0	O_2(g)	0
Br_2(ℓ)	0	Cu(s)	0	LiBr(s)	−351.2	O_3(g)	142.67
C(s, dia)	1.897	F_2(g)	0	LiCl(s)	−408.27	PH_3(g)	22.89
C(s, gra)	0	Fe(s)	0	LiF(s)	−616.0	Pb(s)	0
CCl_4(ℓ)	−128.4	$Fe_2(SO_4)_3$(s)	−2,583.00	LiI(s)	−270.4	$PbCl_2$(s)	−359.41
CH_2O(g)	−115.90	Fe_2O_3(s)	−825.5	Mg(s)	0	PbO_2(s)	−274.47
CH_3COOH(ℓ)	−483.52	Ga(s)	0	MgO(s)	−601.60	$PbSO_4$(s)	−919.97
CH_3OH(ℓ)	−238.4	HBr(g)	−36.29	NH_3(g)	−45.94	Pt(s)	0
CH_4(g)	−74.87	HCl(g)	−92.31	NO(g)	90.29	S(s)	0
CO(g)	−110.5	HF(g)	−273.30	NO_2(g)	33.10	SO_2(g)	−296.81
CO_2(g)	−393.51	HI(g)	26.5	N_2(g)	0	SO_3(g)	−395.77
C_2H_5OH(ℓ)	−277.0	HNO_2(g)	−76.73	N_2O(g)	82.05	SO_3(ℓ)	−438
C_2H_6(g)	−83.8	HNO_3(g)	−134.31	N_2O_4(g)	9.08	Si(s)	0
C_6H_{12}(ℓ)	−157.7	H_2(g)	0	N_2O_5(g)	11.30	U(s)	0
$C_6H_{12}O_6$(s)	−1277	H_2O(g)	−241.8	Na(s)	0	UF_6(s)	−2,197.0
C_6H_{14}(ℓ)	−198.7	H_2O(ℓ)	−285.83	NaBr(s)	−361.1	UO_2(s)	−1,085.0
$C_6H_5CH_3$(ℓ)	12.0	H_2O(s)	−292.72	NaCl(s)	−385.9	Xe(g)	0
C_6H_6(ℓ)	48.95	He(g)	0	NaF(s)	−576.6	Zn(s)	0
$C_{10}H_8$(s)	77.0	Hg(ℓ)	0	NaI(s)	−287.8	$ZnCl_2$(s)	−415.05
$C_{12}H_{22}O_{11}$(s)	−2,221.2						

Sources: National Institute of Standards and Technology's Chemistry WebBook(opens in new window); D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 89th ed. (Boca Raton, FL: CRC Press, 2008); J. A. Dean, ed., Lange's Handbook of Chemistry, 14th ed. (New York: McGraw-Hill, 1992).

Example 7.7.3

Show that the reaction

$$\mathrm{Fe_2O_3(s)+3\,SO_3(g)\rightarrow Fe_2(SO_4)_3(s)}$$

can be written as a combination of formation reactions.

Solution

There will be three formation reactions. The one for the products will be written as a formation reaction, while the ones for the reactants will be written in reverse. Furthermore, the formation reaction for SO_3 will be multiplied by 3 because there are three moles of SO_3 in the balanced chemical equation. The formation reactions are as follows:

$$Fe_2O_3(s)\rightarrow 2Fe(s)+\frac{3}{2}O_2(g)$$

$$3\times\left[SO_3(g)\rightarrow S(s)+\frac{3}{2}O_2(g)\right]$$

$$\mathrm{2\,Fe(s)+3\,S(s)+6\,O_2(g)\rightarrow Fe_2(SO_4)_3(s)}$$

When these three equations are combined and simplified, the overall reaction is

$$\mathrm{Fe_2O_3(s)+3\,SO_3(s)\rightarrow Fe_2(SO_4)_3(s)}$$

Exercise 7.7.3

Write the formation reactions that will yield

$$2\,SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g).$$

Answer

$$2 \times [SO_2(g) \rightarrow S(s) + O_2(g)]$$
$$2 \times \left[S(s) + \frac{3}{2}O_2(g) \rightarrow 2SO_3(g)\right]$$

Now that formation reactions have been established as the major type of thermochemical reaction being examined in this chapter, is it necessary to write all of the formation reactions when the aim is to determine the enthalpy change of any random chemical reaction? No. There is an easier way. You may have noticed in all of our examples that signs are changed on the enthalpies of formation of the reactants, and signs are not changed on the enthalpies of formation of the products. We also multiply the enthalpies of formation of any substance by its coefficient—technically, even when it is just 1. This allows us to make the following statement: *the enthalpy change of any chemical reaction is equal to the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants*. In mathematical terms,

$$\Delta H_{rxn} = \sum n_p \Delta H_{f,p} - \sum n_r \Delta H_{f,r}$$

where n_p and n_r are the number of moles of products and reactants, respectively (even if they are just 1 mol), and $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the enthalpies of formation of the product and reactant species, respectively. This *products-minus-reactants* scheme is very useful in determining the enthalpy change of any chemical reaction, if the enthalpy of formation data are available. Because the mol units cancel when multiplying the amount by the enthalpy of formation, the enthalpy change of the chemical reaction has units of energy (joules or kilojoules) only.

Example 7.7.4

Use the products-minus-reactants approach to determine the enthalpy of reaction for

$$\begin{array}{lccccc} & 2HBr(g) + & Cl_2(g) \rightarrow & 2HCl(g) + & Br_2(l) & \\ \Delta H_f & -36.3 & 0 & -92.3 & 0 & kJ/mol \end{array}$$

Solution

The enthalpies of formation are multiplied by the number of moles of each substance in the chemical equation, and the total enthalpy of formation for reactants is subtracted from the total enthalpy of formation of the products:

$$\Delta H_{rxn} = \left[\left(2\,\cancel{mol}\right)\left(-92.3kJ/\,\cancel{mol}\right) + \left(1\,\cancel{mol}\right)\left(0kJ/\,\cancel{mol}\right)\right]$$
$$-\left[\left(2\,\cancel{mol}\right)\left(-36.3kJ/\,\cancel{mol}\right) + \left(1\,\cancel{mol}\right)\left(0kJ/\,\cancel{mol}\right)\right]$$

All the mol units cancel. Multiplying and combining all the values, we get

$\Delta H_{rxn} = -112.0$ kJ

Exercise 7.7.4

What is the enthalpy of reaction for this chemical equation?

$$\begin{array}{lccccc} & CO(g) \;+ & H_2O(l) \rightarrow & CO_2(g) + & H_2(g) & \\ \Delta H_f & -110.5 & -285.8 & -393.5 & 0 & kJ/mol \end{array}$$

Answer

+2.8 kJ

Food and Drink Application: Calories and Nutrition

Section 7.2 mentioned the connection between the calorie unit and nutrition: the calorie is the common unit of energy used in nutrition, but we actually consider the kilocalorie (spelled Calorie with a capital C). A daily diet of 2,000 Cal is actually 2,000,000 cal, or over 8,000,000 J, of energy.

Nutritionists typically generalize the Calorie content of a food by separating it into the three main components: proteins, carbohydrates, and fats. The general rule of thumb is as follows:

Table with two columns and three rows. The first (left) column is labeled "If the food is..." and the second (right) column two is labeled "It has this energy content...". Underneath the first column, in the rows are different food components. Underneath the second column, in the rows are the calories for the different corresponding food in the left rows.

If the food is...	It has this energy content...
protein	4 Cal/g
carbohydrate	4 Cal/g
fat	9 Cal/g

This table is very useful. Assuming a 2,000 Cal daily diet, if our diet consists solely of proteins and carbohydrates, we need only about 500 g of food for sustenance—a little more than a pound. If our diet consists solely of fats, we need only about 220 g of food—less than a half pound. Of course, most of us have a mixture of proteins, carbohydrates, and fats in our diets. Water has no caloric value in the diet, so any water in the diet is calorically useless. (However, it is important for hydration; also, many forms of water in our diet are highly flavored and sweetened, which bring other nutritional issues to bear.)

When your body works, it uses calories provided by the diet as its energy source. If we eat more calories than our body uses, we gain weight—about 1 lb of weight for every additional 3,500 Cal we ingest. Similarly, if we want to lose weight, we need to expend an extra 3,500 Cal than we ingest to lose 1 lb of weight. No fancy or fad diets are needed; maintaining an ideal body weight is a straightforward matter of thermochemistry—pure and simple.

Key Takeaways

- A formation reaction is the formation of one mole of a substance from its constituent elements.
- Enthalpies of formation are used to determine the enthalpy change of any given reaction.